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Key Points:
- The removal of TOC by water abstraction represents 1.5% of the total removal rate across UK watersheds
- The emissions factor for 1 tonne of organic carbon entering the UK fluvial network has a median value of 3.01 tonnes CO2eq/yr
- Globally, a per capita values for countries with municipal treated water supply would be 0.8–0.86 kg C/ca/yr

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The role of water treatment abstraction in the flux and greenhouse gas emissions from organic carbon and nitrogen within UK rivers

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Abstract The fate of organic matter through watersheds has been shown to be an important component of the global carbon cycle and processes in rivers can rapidly transfer carbon from the terrestrial biosphere to the atmosphere. However, the role of water abstraction in diverting organic matter from freshwater has not been considered. This study used two methods to estimate the amount of organic carbon removed by water treatment processes, first, by estimating the amount of carbon that has to be removed given the abstracted volumes and the freshwater composition; and, second, estimated from reports of the production and composition of water treatment residuals from water companies. For the UK, the median total organic carbon removed by water abstraction was 46 ktonnes C/yr, this equates to a median per capita value of 0.76 kg C/ca/yr. The median total organic nitrogen removed was 4.0 ktonnes N/yr, equivalent to 0.07 kg N/ca/yr. The removal of TOC by water abstraction represents 1.5% of the total removal rate across UK watersheds. The release of greenhouse gases from UK rivers is now estimated to be between 12,754 and 32,332 ktonnes CO_{2eq}/yr equivalent to between 55 and 127 tonnes CO_{2eq}/km^2/yr with fluvial organic matter between 8800 and 15,116 ktonnes CO_{2eq}/yr in the proportion 6:86:8 N_2O:CO_2:CH_4. The emissions factor for 1 tonne of organic carbon entering the UK fluvial network has a median value of 2.95 tonnes CO_{2eq}/yr with a 5th to 95th percentile range of 2.55 to 3.59 tonnes CO_{2eq}/yr. Globally, a per capita values for countries with municipal treated water supply would be 0.8 to 0.86 kg C/ca/yr.

1. Introduction

Meybeck [1993] estimated the flux of carbon (dissolved organic carbon, particulate organic carbon, and dissolved inorganic carbon) from the world's rivers to the oceans was around 542 Mtonnes C/yr in proportions 37:18:45 for DOC:POC:DIC, respectively. *Ludwig et al.* [1996] used a spatially explicit model of global fluvial carbon fluxes to suggest fluxes of 800 Mtonnes C/yr with a split of approximately 50:25:25 for DOC:POC:DIC, respectively. These figures provide useful estimates of fluvial carbon losses from the land to the oceans at the tidal limit, but they do not account for in-stream losses along the length of the river, between the carbon sources (e.g., soils) and the ocean. For the global scale, *Cole et al.* [2007] estimated that 1900 Mtonnes C/yr enters rivers of which 800 Mtonnes C/yr (42% of the input) is returned to the atmosphere. *Battin et al.* [2009] used a 21% removal rate for DOC from global rivers and implying that, in comparison to the values suggested by *Cole et al.* [2007], there must be considerable contributions from the loss of POC and DIC. *Regnier et al.* [2013] have estimated that the total global carbon flux (inorganic and organic carbon) into freshwaters was 2800 Mtonnes C/yr of which 1000 Mtonnes C/yr was exported from the tidal limit (i.e., a 64% removal rate). The 2007 Intergovernmental Panel on Climate Change (IPCC) report included an estimate of global DOC flux from rivers [*Solomon et al.*, 2007] but did not consider the effect of in-stream DOC losses, let alone the flux and loss of POC or the degassing of excess CO_2. Previous studies have made the connection between carbon loss from rivers and impact on the atmosphere but did not consider the greenhouse gas losses as the speciation of the carbon loss has not been included. Furthermore, nitrogen losses not been considered. *Worrall et al.* [2016] has extended the assessment of fluvial carbon loss to consider loss of organic matter and the speciation of that loss, i.e., the atmospheric impact of fluvial losses of organic matter will not only be a matter of how much of the organic matter is lost as CO_2 or as CH_4 but also the organic matter will release N, and therefore has the potential to release N_2O to the atmosphere.

Most studies have used a mass balance approach to assess fluvial carbon losses. *Worrall et al*. [2012a] measured the net watershed loss of DOM across the UK and found a value of 78% and it was assumed that this was loss to the atmosphere. Similarly, *Worrall et al*. [2014] showed that according to mass balance there was 20% loss of POM across UK catchments. In both these cases, the net watershed loss was equated with the loss to atmosphere; however, in the case of POM the net watershed loss could be ascribed to in-channel storage [e.g., *Collins and Walling*, 2007] or to floodplain storage [*Walling et al*., 1999] rather than turnover to the atmosphere. *Worrall et al*. [2016] accounted for in-channel and floodplain storage in their assessment of the fluvial organic matter losses with a maximum of 3% loss of POM to in-channel and floodplain storage. However, in none of the studies [e.g., *Regnier et al*., 2013, *Worrall et al*., 2016] was an allowance made for the role for water abstraction for drinking water in removing fluvial organic carbon, yet in water treatment the removal of particles (which would include POM) and the flocculation of DOM are essential processes prior to disinfection and supply of clean water. Therefore, the aim of this study was to assess the proportion of fluvial organic matter that is lost through water abstraction in the context of the greenhouse gas emissions of rivers.

2. Approach and Methodology

This study took two approaches to estimate the role of water treatment abstraction on the fate of fluvial carbon. First, analysis of fluvial carbon in river, reservoir, and ground-water were coupled with water abstraction data to calculate the amount of carbon that would have to be removed to supply the known volume of water. Second, water industry data on the production of water treatment residues (WTR) were coupled with analysis of those water treatment residues to understand the amount of carbon diverted. The greenhouse gas emissions will consider CO_2, CH_4, and N_2O.

2.1. Water Abstraction

Total water abstracted; the proportion of the total abstraction coming from groundwater; and the number of customers supplied for each UK water company for the period 2008–2014 were available from (http://www.water.org.uk/). The values of water abstraction are reported without uncertainty and were used as such within this study.

The DOC concentration that would have to be removed in water treatment was estimated from the distribution of DOC concentrations in surface and ground waters. Records of DOC concentration from England, Wales, Scotland, and Northern Ireland were obtained from the national environmental monitoring agencies (Environment Agency; Natural Resources Wales; Scottish Environmental Protection Agency; and Northern Ireland Environment Agency). Records for the period 2005 to current were examined and for all freshwater samples (i.e., no marine or estuarine samples were included) and excluding any samples that were for individual waste effluent streams; named pollution sources or from known pollution incidents. The DOC concentration data were divided between surface and groundwater results as it was possible to relate these water types to water sources abstracted by the UK water companies—there was no consistent data on the proportion of reservoir versus river sources for each water company. The distribution of the DOC data, divided by surface and groundwater results, were tested using the Anderson-Darling test [*Anderson and Darling*, 1952] and log-transformed and retested. Neither the surface nor the groundwater DOC, whether log-transformed or not, were normally distributed and the reason for this was because neither parametric distribution could account for the large numbers of data close to zero which must correspond to the limit of detection. There are several ways of dealing with data below a reported limit of detection [e.g., *Palarea-Albaladejo and Martin-Fernandez*, 2013], and in this study we take the approach of using a nonparametric distribution.

The monitored DOC concentration data were divided between regions. For Northern Ireland and Scotland, the water company regions precisely coincide with the reporting regions for water quality monitoring, but for England and Wales water company areas do not precisely coincide with monitoring reporting regions but there is a close approximation (Figures 1 and 2). So the abstraction values for surface and ground water for each water company could be associated with regionally specific monitoring data for DOC in surface and ground waters. The monitoring data could not be associated with individual abstractions.

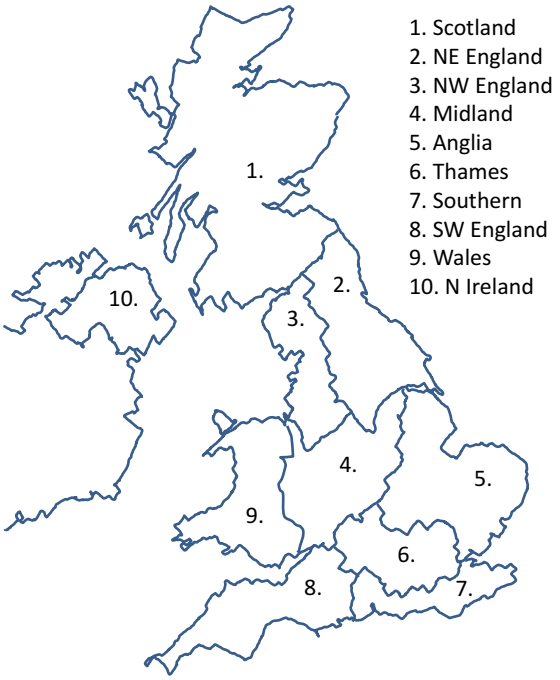

Figure 1. The monitoring regions for DOC and POC used by this study for the UK.

Since water abstraction are reported annually, the DOC concentration data for each of surface and ground water for each monitoring region were summarized (because of the distribution of the data) as the median and 90th percentile range for the period 2005 to current: it is assumed that DOC concentrations were stationary over this period, i.e., DOC concentration across the UK showed no significant trend within this time. Given the range of DOC concentrations that could be expected, the amount of DOC that then had to be extracted was simply the stochastic combination of the water abstraction for each company and its respective DOC concentration range. For this study, 100 realizations were performed for the annual amount of DOC diverted from rivers by water abstraction based upon selecting values at random assuming a uniform distribution defined by the uncertainty in each variable. The DON removal was assessed from a knowledge of the C/N ratio as discussed below.

Water abstracted from surface water sources will also contain carbon from particulate organic matter (POM) and so the diversion of POM by water abstraction needs to be calculated. This study has assumed that the POM concentration of groundwater was zero for all water supply sources. Particulate organic matter is not measured directly by any UK monitoring agency but suspended sediment concentration and its ash content have been monitored making an estimate of the POM concentration possible (i.e., POM concentration = suspended sediment concentration – ash content). However, there were no ash content data reported for Scotland or Northern Ireland and there was only 960 measurements made after 2005,

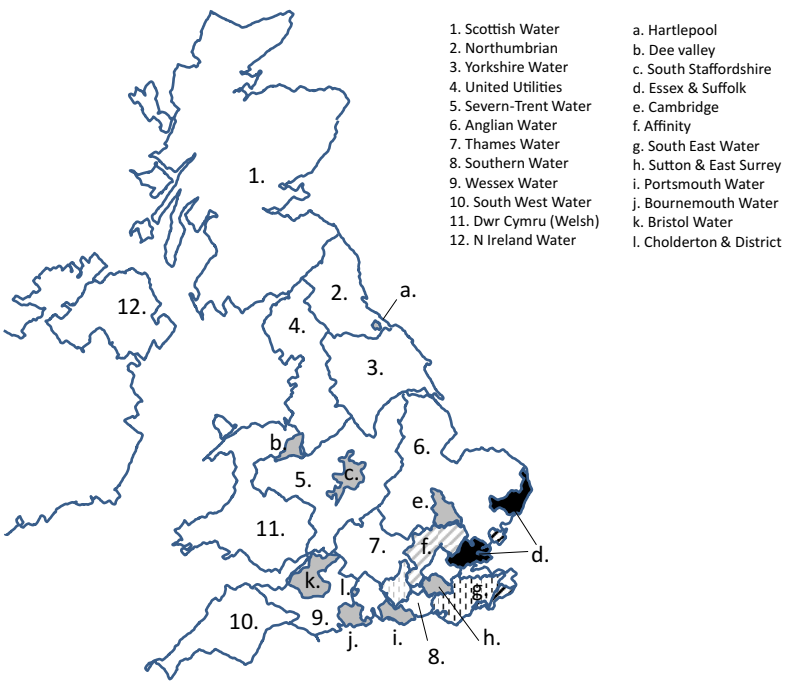

Figure 2. The water and sewage services companies (1 through 12) and the water supply only companies (a through to l).

Table 1. The Average Water Abstraction, Population Served; and the Proportion of Surface Versus Groundwater Sources Abstracted[a]

Water Company	Water Abstracted (ML/d)	Population Served (ca)	Proportion of Water Abstracted From Groundwater	Consumption (ML/ca/d)
Anglian	1045	4,401,000	0.3	237
Welsh	741	2,970,000	0.03	249
Northumbrian	667	1,035,000	0.2	643
Essex & Suffolk	429	1,665,000	0.3	258
Severn Trent	1566	7,850,000	0.33	200
Southern	495	2,385,000	0.7	208
South West	372	1,679,000	0.2	221
Thames	2235	9,067,000	0.7	246
United Utilities	1498	6,968,000	0.2	215
Wessex	294	1,263,000	0.2	233
Yorkshire	1096	4,889,000	0.2	224
Bournemouth	135	434,000	0.3	311
Bristol	241	1,165,000	0.3	207
Cambridge	68	318,000	0.3	214
Dee Valley	57	261,000	0.17	219
Portsmouth	158	674,000	0.7	234
South East	306	2,058,000	0.3	149
South Staffordshire	257	1,283,000	0.3	201
Sutton and East Surrey	149	655,000	0.3	227
Affinity	809	3,486,000	0.3	232
Northern Ireland	562	795,000	0.08	706
Scottish	1300	5,090,000	0.05	255
UK total	144,880	59,113,000	0.31	239

[a]The Hartlepool Water Company was included with Northumbrian; and the Cholderton and District Water Company are included on Figure 2 but currently supplies no more than 2500 people.

therefore values for Wales and English regions were summarized (median, 5th and 95th percentile) from 1974. Again the assumption of stationarity was made, but, it should be noted that *Worrall et al*. [2014] had a found small yet significant increase in UK fluvial POM concentrations since 1974 to present and for the same data set as used by this study. However, since the POM concentration has been observed to be increasing the assumption made here is a conservative one and would, if anything, underestimate the role of abstraction in diverting POM. Equally, the POM data were tested for normality, both log-transformed and untransformed, using the Anderson-Darling test and as a result a nonparametric approach was used. For the POM, concentration is not the POC concentration and it was assumed that POC content was between 45 and 50% of the POM [*Moody et al*., 2013], this distribution was taken as uniform for purposes of uncertainty analysis.

Worrall et al. [2014] estimated POC and PON from POM given that the organic carbon content of organic matter was between 45 and 50% and that the average C/N ratio of suspended sediment in the UK was 8.1 ± 5.2 ($n = 13$) [*Hillier*, 2001]. Alternatively, *Worrall et al*. [2014] used POM data collected as part of the LOIS project [*Neal and Davies*, 2003]. The LOIS project collected 2484 samples for POM across 5 years for the Humber Basin (26,109 km^2; 17% of the UK catchment area). Across 5 years (1994–1998) and 16 sites across 13 rivers (Rivers Aire, Calder, Derwent, Don, Great Ouse, Nidd, Yorkshire Ouse, Swale, Trent, Tweed, Ure, Wear, and Wharfe—*Robson and Neal* [1997]), the median POC/PON C/N ratio was 11.5 with a 5th to 95th percentile range of 6.7–21.4—as for DOC and POM normality tests showed that a nonparametric distribution would be preferred. *Worrall et al*. [2016] reviewed literature data (cf. Table 1) and found a geometric mean for non-UK catchments of 10.3. The discharge-weighted average from the review of *Ittekkot and Zhang* [1989] was 10.7 and for the LOIS data the geometric mean was 11.7. The concentration of DON was not measured in the LOIS and so for consistency with previous studies [e.g., *Worrall et al*., 2016] the values for the C/N of POM were used for the C/N of DOM.

2.2. Water Treatment Residues (WTR)

The amount of WTR produced by water companies provides an alternative measure of the amount of carbon diverted. The WTR is created from a range of processes within water treatment but in general can be divided between iron and aluminium-based WTR depending upon the salt used for flocculation and coagulation but the residues will also include wastes from a range of screening and filtration processes. The water treatment process will often be facilitated by addition of organic coagulation aids typically polyacrylamide and modified starch and so the organic matter present in the WTR will not all be from the abstracted water (1% of carbon content—*Johnson et al*. [2015]). Values of the production of WTR for the UK water industry were taken from industry reports and from global literature.

In addition, samples of WTR were taken from nine local water treatment works in the north east of England. Samples of WTR were collected four times during 1 year (October 2011, January, 2012, May 2012, and August 2012) from nine water treatment works across the Northumbrian Water region (Figure 1). Five of the

works were based on river abstraction and four on reservoir sources, but none with groundwater sources as there none within the region. Four of the sites used aluminium-based coagulant and five used iron-based coagulants. The sampled WTR from each site for each season was analyzed for its water content, loss on ignition, and elemental composition of C and N.

For water content measurement, triplicate subsamples were weighed into ceramic crucibles and dried to constant mass at 105°C. The triplicate oven-dried subsamples were then transferred to a muffle-furnace and then heated at 550°C for 4 h to give the loss on ignition. For the elemental composition, triplicate subsamples were freeze-dried, ball-milled, and analyzed for C and N composition on COSTECH 4010 elemental combustion system. The elemental analyzer was run in dual reactor mode, chromium oxide/silvered cobalt reactor at 950°C and reduction copper at 650°C. The carrier gas was helium and sulfanilamide was used to give a 5 point calibration.

2.3. Upscaling of the Results

The results for UK water abstraction were placed in the context of the current best estimate of the organic matter budget of UK rivers [*Worrall et al*., 2016]. The most recent estimate of the UK fluvial carbon budget had included the potential for storage within river channels or floodplains but had not included an uncertainty analysis nor had it considered the possibility of diversion by water abstraction. The total flux of organic carbon to the atmosphere for the UK is:

$$C^{atm} = C^{s}_{DOC} - C^{tl}_{DOC} - C^{abs}_{DOC} + C^{s}_{POC} - C^{tl}_{POC} - C^{abs}_{POC} - C^{ic}_{POC} - C^{fp}_{POC} + C^{s}_{CO2} \quad (1)$$

where: C^{x}_{y} = the flux of organic carbon in form of x from or to y, where x = DOC is dissolved organic carbon, POC is particulate organic carbon, and CO_2 is the excess dissolved CO_2; and where y = *atm* is flux to the atmosphere, *s* is the flux from the terrestrial source to the fluvial network, *tl* is the flux from the tidal limit to the continental shelf, *ic* is the flux to in-channel storage, *fp* is the flux to floodplain storage, and *abs* is the flux via abstraction.

The flux of excess CO_2 through and from the area of England and Wales was estimated, with uncertainty, by *Worrall et al*. [2007]; however, this uncertainty was not used in subsequent analyses [e.g., *Worrall et al*., 2014], and therefore that uncertainty estimate was included in this analysis. The uncertainty in the estimate of national excess CO2 flux was given as an interquartile range of ±15% and this was taken as the bounds of a uniform distribution. Because of the way in which dissolved CO_2 was calculated in *Worrall et al*. [2007], it is the excess above that which would be in equilibrium with the atmosphere and so it could all be expected to be lost to the atmosphere within the fluvial network.

The fluxes of DOC at the tidal limit (C^{tl}_{DOC}) were taken from *Worrall et al*. [2012a] as updated by *Worrall et al*. [2016] where in the latter the data from 2003 to 2012 were used—and the method used had a published uncertainty of ±15%: this uncertainty estimate was based upon the method of *Worrall and Burt* [2007] as the interquartile range and this estimation was used here as the limits of uniform distribution. The net watershed losses of DOC ($C^{atm}_{DOC} + C^{abs}_{DOC}$) and the flux of DOC from the terrestrial source to the fluvial network (C^{s}_{DOC}) was also estimated in *Worrall et al*. [2012a] (as updated in *Worrall et al*. [2016]) but no uncertainty in these estimates was used further. For this study, the standard errors of the fit of the equations derived in *Worrall et al*. [2012a] were used for error estimation on C^{s}_{DOC} and $C^{atm}_{DOC} + C^{abs}_{DOC}$ and the C^{atm}_{DOC}, and its uncertainty, were then calculated by difference. Because the uncertainty in C^{s}_{DOC} and $C^{atm}_{DOC} + C^{abs}_{DOC}$ was based on fit of the linear equation the uncertainty in these terms was assumed to be normally distributed.

Worrall et al. [2014] estimated the flux of POC at the tidal limit (C^{s}_{POC}) and as above the method used had a published uncertainty of ±15% (interquartile range and assumed to be uniformly distributed for the purpose of this study). *Worrall et al*. [2014] assumed that the net watershed losses POC were made up of: floodplain storage (C^{fp}_{POC}); in-channel storage (C^{ic}_{POC}); and turnover to the atmosphere (C^{atm}_{POC}); and so in this study diversion to water treatment was also included (C^{abs}_{POC}). The uncertainty in the extent of floodplain storage (C^{fp}_{POC}) and in-channel storage (C^{ic}_{POC}) were taken from *Worrall et al*. [2016] with in-channel storage taken as between 1 and 2% of the POM flux and the floodplain storage taken to be no greater than 1% of the POM flux—in both cases the distribution in these ranges was assumed to be uniform because of the absence of distributional information. As for DOC, the uncertainty in the net watershed loss in POM was based on fit of

the linear equations derived in *Worrall et al*. [2014], the uncertainty in that term was assumed to be normally distributed.

The fluvial losses of nitrogen to the atmosphere would not only be a matter of the organic nitrogen species but also the inorganic species:

$$N^{atm} = N^{s}_{DON} - N^{tl}_{DON} - N^{abs}_{DON} + N^{s}_{PON} - N^{tl}_{PON} - N^{abs}_{PON} - N^{ic}_{PON} - N^{fp}_{PON} + N^{s}_{NO3} - N^{tl}_{NO3} + N^{s}_{NH4} - N^{s}_{NH4} \quad (2)$$

where N^{x}_{y} = the flux of nitrogen in form of x from or toy, where x = DON is dissolved organic nitrogen, PON is particulate organic nitrogen, NO3 is nitrate; and NH4 is ammonium; and where y is as for equation (1).

The estimates of terrestrial biosphere sources losses; the loss at the tidal limit; and the net watershed loss for nitrate, DON and ammonium (e.g., N^{tl}_{NH4}) were taken from the study of *Worrall et al*. [2012b] with the uncertainty in each being estimated in this study as per DOC fluxes above, i.e., estimated from the standard errors of the fits of the equations derived within the previous study. The estimates of PON flux at the tidal limit (N^{tl}_{PON}); from the terrestrial source (N^{s}_{PON}) and its net watershed losses with the concomitant uncertainties in each were taken from the analysis of *Worrall et al*. [2014]. In *Worrall et al*. [2014], it was assumed that net watershed loss was $N^{s}_{PON} - N^{tl}_{PON} = N^{atm}_{PON}$, as with the carbon species the net watershed loss was now assumed to be $N^{s}_{PON} - N^{tl}_{PON} = N^{atm}_{PON} + N^{ic}_{PON} + N^{fp}_{PON}$ with the uncertainties in N^{ic}_{PON} and N^{fp}_{PON} calculated as for POC and then the magnitude and uncertainty in N^{atm}_{PON} were calculated by difference. For the calculation of DON and PON fluxes or losses, the additional uncertainty is in the value of the C/N ratio and its median the interquartile range as defined above was used (11.2, between 9.2 and 14.3).

The fluvial nitrogen and carbon budgets are not, however, the fluvial GHG budget although the fluvial carbon budget has often been mistaken for such [*Van Oost et al*., 2007]. The added complexity for calculating a greenhouse budget are the greenhouse gas warming potentials of the different C and N species that could be released. Carbon could be released as either CO_2 or CH_4 with the latter having a far higher GWP. The GWP of rivers becomes:

$$F^{atm} = K_{CO2} P_{CO2} C^{atm} + K_{CH4}(1 - P_{CO2}) C^{atm} + K_{N2O} P_{N2O} N^{atm} \quad (3)$$

where K_x = the greenhouse gas warming potential of x where x is CO_2, CH_4, or N_2O; and P_y = the proportion of the loss that is lost as y, with y as CO_2 or N_2O. The proportion of CO_2 to CH_4 produced in fluvial carbon turnover was based on literature review of *Worrall et al*. [2016] and taken as being uniformly distributed between 0.64 and 2.2% [*Striegl et al*., 2012; *Silvennoinen et al*., 2008]. Similarly, the nitrogen can be released as either N_2 or N_2O with the latter being a very powerful greenhouse gas, the proportion of N_2O to N_2 produced was taken as being uniformly distributed between 0.3 and 3% [*Baulch et al*., 2011]. Previous studies have assumed that once organic matter has entered storage (i.e., overbank or in-channel sediment) that it is lost from the atmosphere and the same assumption was made in this study although the implications of such an assumption will be discussed below.

Given the uncertainty in each pathway, the difference is judged stochastically with 100 values selected at random from each pathway assuming the distribution of each pathway as defined for each above.

Furthermore, UK data were viewed in the light of global data for the composition of WTR; the production of WTR; and water abstraction.

3. Results

The average abstraction volumes for UK water companies are given in Table 1.

There were 60,020 data for the DOC concentration in groundwater from 4176 sampling locations for the UK between 2005 and 2015 with a median of 0.7 mg C/L (5th to 95th percentile range—0.2–3.8 mg C/L). There were 145,320 (42,788 from Scotland) data coming from 4326 locations (1151 from Scotland) for DOC in surface water between 2005 and 2015 with median concentration 4.4 mg C/L (5th–95th percentile range—1.1–13.0 mg C/L): regional variation is given in Table 2. Within the surface water samples, there were 26,770 samples from 754 lakes and reservoirs (450 in Scotland) and these had a median of 3.8 mg C/L (5th to 95th percentile range—1.3–13.6 mg C/L) and the river and stream samples had a median of 4.6 mg C/L (5th to 95th percentile range—1.2–13.4 mg C/L).

Table 2. The Distribution of DOC Concentration for Each UK Monitoring Region for the Period 2005 to 2014 by Surface or Groundwater[a]

Region	Source Water	Median (mg C/L)	5th to 95th Percentile Range (mg C/L)	Water Company
NE England	Groundwater	1.2	0.2–3.9	Northumbrian and Yorkshire
	Surface water	5.4	2.0–14.4	
Southern	Groundwater	3.5	0.3–10.0	Southern; South East;
	Surface water	5.1	1.2–11.2	Sutton and East Surrey and Portsmouth
Thames	Groundwater	0.8	0.3–3.0	Thames
	Surface water	1.5	0.3–7.7	
Anglia	Groundwater	1.0	0.4–4.0	Anglian, Affinity, Cambridge,
	Surface water	5.3	2.5–13.6	Essex and Suffolk
Wales	Groundwater	0.7	0.2–5.3	Dwr Cymru
	Surface water	2.7	0.8–8.9	
Midland	Groundwater	0.7	0.2–3.8	Severn Trent and
	Surface water	5.2	1.7–9.9	South Staffordshire
NW England	Groundwater	0.8	0.2–7.0	United Utilities and
	Surface water	4.4	0.6–14.9	Dee valley water
SW England	Groundwater	0.6	0.2–2.0	South West, Wessex.
	Surface water	2.5	0.8–8.5	Bournemouth, and Bristol
Northern Ireland	Groundwater	1.9	0.6–1.4[b]	N. Ireland
	Surface water			
Scotland	Groundwater	1.2	0.3–3.3[c]	Scottish
	Surface water	5.4	2.0–17.9	
UK total	Groundwater	0.7	0.2–3.8	
	Surface water	4.2	1.1–13.0	

[a]UK total values are given as median and 5th to 95th percentile range.
[b]Based on only nine samples.
[c]Based on only five samples.

When distributed across the ground and surface water abstractions of the UK the median estimate of the amount of DOC removed is 28 ktonnes C/yr (5th–95th percentile range—11–44 ktonnes C/yr) which is 0.42 kg C/ca/yr (5th–95th percentile range—0.18–0.72 kg C/ca/yr). Given the ranges reported for the C/N of DOM, then the amount nitrogen removed in the removal of DOM by water abstraction was 2.3 ktonnes N/yr (5th–95th percentile range—0.8–3.8 ktonnes N/yr) or 0.04 kg N/ca/yr (5th–95th percentile range—0.01–0.06 kg N/ca/yr).

There were 35,490 POM measurements from 198 sites across the England and Wales from 1974 to 2014. The median POM concentration was 4.6 mg/L (5th–95th percentile range—0.5–23 mg/L) giving a median POC of 2.2 mg C/L (5th–95th percentile range–0.2 to 11 mg C/L): regional variation is given in Table 3. When distributed across the surface water abstractions of the UK, the amount of POC removed from the river system by water abstraction had a median of 19 ktonnes C/yr (5th–95th percentile range of 4–31 ktonnes C/yr) which given the size of the population supplied was 0.32 kg C/ca/yr (with a 5th–95th percentile range of 0.07–0.53 kg C/ca/yr). Given the ranges reported for the C/N of POM, then the amount of nitrogen removed in particles had a median estimate of 1.5 ktonnes N/yr (0.4–2.8 ktonnes N/yr) or 0.02 kg N/ca/yr (0.001–0.05).

Table 3. The Distribution of POC Concentration for Each UK Monitoring Region for the Period 2005–2014 by Surface or Groundwater

Region	Median (mg C/L)	Range (mg C/L)
NE England	2.4	0.2–11.4
Southern	1.8	0.4–8.0
Thames	3.3	1.4–10.7
Anglia	2.9	0.5–9.0
Wales	1.8	0.0–15.4
Midland	3	0.5–10.0
NW England	3.5	0.5–13.0
SW England	1.4	0.2–10.3
UK total	2.2	0.2–11.0

The total organic carbon removed by water abstraction has a median estimate of 46 ktonnes C/yr (5th–95th percentile range of 22–67 ktonnes C/yr) equivalent 0.76 kg C/ca/yr (5th–95th percentile range of 0.18–1.11 kg C/ca/yr). The total organic nitrogen removed by water abstraction 4.0 ktonnes N/yr (5th–95th percentile range of 1.7–5.8 ktonnes N/yr) equivalent 0.07 kg C/ca/yr (5th–95th percentile range of 0.03–0.1 kg C/ca/yr).

3.1. WTR Residues

Results of characterization of the WTR are given in Table 4. For the Northumbrian Water company,

Table 4. Composition of the WTR Measured for Northeast England Water Treatment Works

Treatment Works	Coagulant	Dry Solids (%)	LOI (%)	C (%)	N (%)
Horsley	Al/Fe	26	44	16.7	0.7
Gunnerton	Al	22	66	25.0	0.7
Warkworth	Al	21	41	14.0	0.6
Whittle Dene	Al	19	51	18.2	0.9
Broken Scar	Fe	19	37	15.4	0.6
Fontburn	Fe	17	49	22.7	0.7
Honey Hill	Fe	17	51	23.4	0.7
Lartington	Fe	19	50	22.4	0.8
Mosswood	Fe	20	48	21.4	0.8
Total		19	50	21.4	0.7

region between 2010 and 2014 annual production of WTR was between 55,966 and 69,666 wet tonnes/yr which given the median results of the WTR residues suggests that between 2.1 and 2.7 kg C/ca/yr were removed. *Bolto and Gregory* [2007] suggest optimum dosage of flocculent as 1 mg polymer/1 g of suspended solids. The sites sampled by this study all used polyacrylamide as flocculent aid and 1 mg of polyacrylamide contains 51% C and 20% N by mass.

When compared to values gleaned from the literature (Table 5), the values from north east of England were at the higher end of the range reported from the United States and this could reflect the drinking water of the north east of England being dominantly sourced from peat-covered catchments and that peat-covered catchments are strong sources of DOC [*Aitkenhead et al*., 1999].

At the UK scale values of the estimated WTR production have been between 131,000 and 182,000 tonnes dry weight [*Babatunde and Zhao*, 2007] which given the composition measured gives a 0.43 and 0.60 kg C/ca/yr or between 26 and 36 ktonnes C/yr. It is not too surprising that values for the Northumbrian Water region are greater than that for the UK as a whole given the high DOC values for the region (Table 2).

3.2. Upscaling of Results

The fluvial flux of carbon from the UK is detailed in Table 6 and summarized in Figure 3. The study would now estimate the flux of organic carbon from the UK terrestrial biosphere to the river network as between 3910 and 5521 ktonnes C/yr which equates to between 16.0 and 22.6 tonnes C/km^2/yr. The amount of carbon loss to the atmosphere was estimated to between 2077 and 3643 ktonnes C/yr (equivalent to 8.5 and 14.9 tonnes C/km^2/yr). Note that there is a mismatch in unit of export between the components of interest with some fluxes better expressed per unit area while diversion to water abstraction is better expressed per capita.

The fluvial flux of N from the UK is detailed in Table 7 and Figure 4. The previous estimate of the nitrogen flux from the UK's terrestrial biosphere was 2209 ktonnes N/yr [*Worrall et al*., 2012b] and now that would be estimated as between 1655 and 2721 ktonnes N/yr with storage being between 6.7 and 11.2 ktonnes N/yr and the total N lost to the atmosphere as between 838 and 1889 ktonnes N/yr.

When the greenhouse gas flux was considered, then the total flux from the fluvial network was between 13,222 and 31,920 ktonnes CO_{2eq}/yr (Table 8) in proportion 48:47:5 N_2O:CO_2:CH_4. The UK GHG inventory gives the total greenhouse flux from the UK in 2014 as 455.3 Mtonnes CO_{2eq} and that figure does not include the influence of the rivers. The total figure is comprised of between 2638 and 19,937 ktonnes CO_{2eq}/yr as N_2O; between 442 and 1640 ktonnes CO_{2eq}/yr as CH_4; and between 7551 and 13,186 ktonnes CO_{2eq}/yr as CO_2. When only organic matter is considered, then the contribution from N_2O decreases to between 171 and 1275 ktonnes CO_{2eq}/yr giving the a total GWP of fluvial organic matter of 11,899 (9005 to 15,357) ktonnes CO_{2eq}/yr in proportion 6:85:8 N_2O:CO_2:CH_4. For 2014, the UK government report total greenhouse gas emissions of 514,400 ktonnes CO_{2eq}/yr [*DECC*, 2016], i.e., the greenhouse gas flux from UK rivers represents 2.7% of current UK emissions. The predicted range of organic carbon entering the fluvial network means that the emissions factor for 1 tonnes of organic carbon entering the UK fluvial network has a median value of 3.01 tonnes CO_{2eq}/yr with a 5th–95th percentile range of 2.57–3.45 tonnes CO_{2eq}/yr.

Table 5. Literature Values of WTR Composition

Study	Coagulant	LOI (%)	C (%)	N (%)
Nagar et al. [2009]	Al	33	15	0.6
Elliot et al. [2002]	Al	24.1	19.1	0.73
Sarkar et al. [2007]	Al	46.2	18.8	0.5
Nagar et al. [2009]	Fe	40	21	1.0
Elliot et al. [2002]	Fe	35.6	15.4	0.94
Sarkar et al. [2007]	Fe	47.6	19.6	0.8

Rodriguez et al. [2010] gave values of water treatment residue for the EU as

Table 6. The Summary of the Fluvial Carbon Fluxes for the UK Rivers

Pathway	Median (ktonnes C/yr)	5th to 95th Percentile Range (ktonnes C/yr)
POC flux at source	1106	981–1296
POC loss to storage.	74	54–98
POC loss to atmos.	190	79–291
POC flux at tidal limit	852	752–976
DOC flux at source	3558	2813–4391
DOC loss to storage.	28	14–43
DOC loss to atmos.	2629	1901–3490
DOC flux at tidal limit	904	794–1037
Excess CO_2 loss at source	615	515–695
Excess CO_2 loss to atmos.	615	515–695
TC flux at source	4693	3910–5521
TC loss to storage.	103	76–131
TC loss to atmos.	3435	2731–4256
TC flux at tidal limit	1764	1602–1966

10,000,000 dry tonnes/yr which would give a value 3.96 kg C/ca/yr; however, if this is misreported as dry tonnes and not wet tonnes then the value would be 0.8 kg C/ca/yr, whereas for the United States, the value would be 0.86 kg C/ca/yr.

4. Discussion

Worrall et al. [2014] estimated the POC flux at the tidal limit was 888 ktonnes C/yr with a loss of 20% in transit or 263 ktonnes C/yr and giving a loss at source of 1126 ktonnes C/yr, This POC loss was explained as being due to turnover to the atmosphere; in-channel storage; and deposition on floodplains. *Worrall et al.* [2016] have subsequently estimated the removal rate of in-channel storage to be 1–2% of incoming POC flux and the removal rate due to floodplain deposition was no greater than 1% of the POM flux and proposed that the POM loss to atmosphere was 17% of the POM flux; however, the possibility of removal by water treatment was not considered. This study would now suggest that 1.7% (0.3–2.7%) of the between 0.9 and 1.3% POC lost from the source is lost due to abstraction into water treatment works in addition to the storage in floodplains and the channel. This means that, for the UK diversion of carbon by water abstraction is a more important process than floodplain storage.

The flux of DOC from the terrestrial source is estimated as 3558 ktonnes C/yr with 904 ktonnes C lost at the tidal limit and 2629 ktonnes C/yr lost in transit. The loss in transit was entirely ascribed to loss to the atmosphere but this study would now ascribe 1% of this loss to removal in water abstractions.

When TOC was considered, then the values of WTR removal from the reported production of WTR can be considered, in which case the total amount of TOC removal (DOC + POC removal) for UK rivers would be 2841 ktonnes C/yr (already having subtracted the POM lost to in-channel storage or floodplain deposition), then the amount lost to abstraction would be between 0.9 and 1.3% removal and giving a TOC loss to the atmosphere of between 2077 and 3643 ktonnes C/yr compared to 2400 and 3869 ktonnes C/y based on the abstraction data. The carbon lost in transit could be lost as CO_2 or CH_4.

The above calculations are relative to the river and the assumption is that once the organic matter is removed during water treatment it is no longer atmospherically active relative to its fate in the river. However, energy is required to pump water into a water treatment works and energy is required to remove the

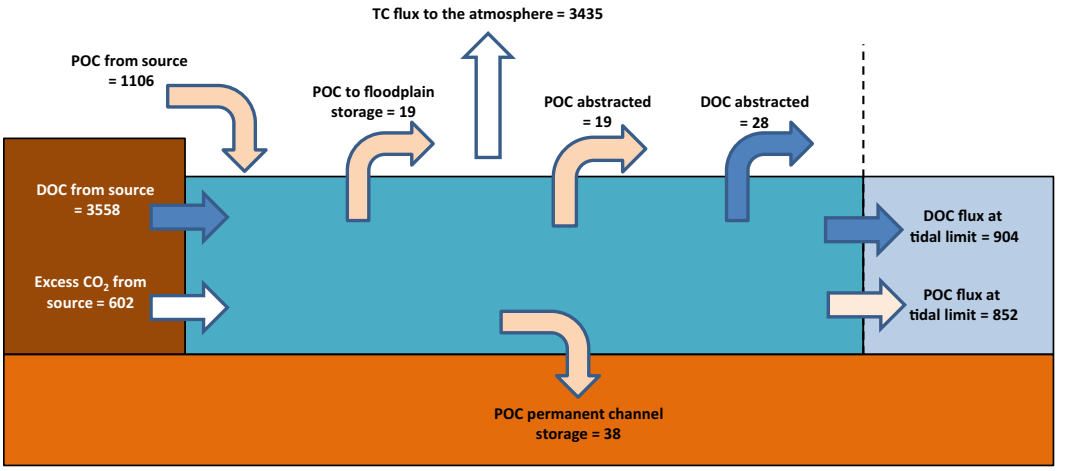

Figure 3. Schematic representation of the fluvial fluxes of carbon into and out of UK rivers based upon median values reported in Table 6.

Table 7. The Fluvial Loss of Nitrogen From the UK

Pathway	Median (ktonnes N/yr)	5th to 95th Percentile Range (ktonnes N/yr)
PON flux at source	231	204 - 264
PON loss to storage.	9	7–10
PON loss to atmos.	46	28–63
PON flux at tidal limit	177	156–204
DON flux at source	205	167–237
DON loss to storage.	2	1–4
DON loss to atmos.	97	68–132
DON flux at tidal limit	103	91–119
NO_3 flux at source	1544	1031–2107
NO_3 loss to atmos.	1164	651–1706
NO_3 flux at tidal limit	398	311–505
NH_3 flux at source	172	137–211
NH_3 loss to atmos.	53	22–77
NH_3 flux at tidal limit	120	92–148
TN flux at source	2170	1656–2721
TN loss to storage.	11	9–13
TN loss to atmos.	1369	838–1889
TN flux at tidal limit	805	703–922

POM and DOM and so the very act of abstracting and treating water creates greenhouse gases. Furthermore, the WTR will itself degrade and produce CO_2. *Jones et al.* [2016] have considered the greenhouse gas emissions resulting from the removal of aquatic carbon for four works treating water from catchments with peat soils. Using only the data for the GHG emissions due to production and chemical use from *Jones et al.* [2016] and not the values for turnover of DOM and POM within works or removed in sludge, then the GHG emissions varied from 11 to 133 tonnes CO_{2eq}/tonne fluvial C removed. The emissions factor of organic carbon entering the fluvial network is between 2.60 and 3.59 tonnes CO_{2eq}/tonne of C entering the river network: therefore abstraction of C via water treatment has many times more atmospheric impact than if it were left in the river network. Given that between 22 and 67 ktonnes C/yr of organic carbon are removed from the UK's fluvial network per year then the treatment of this alone would mean that between 740 and 6768 ktonnes CO_{2eq}/yr with a median = 2904 ktonnes CO_{2eq}/yr are released due to the treatment of organic matter in water. Given the fluxes already observed this would increase the GHG emissions of from fluvial organic carbon to 16,102 ktonnes CO_{2eq}/yr with a 5th–95th percentile range of 11,378–20,461 ktonnes CO_{2eq}/yr and increases the emissions factor to a median of 3.5 tonnes CO_{2eq}/tonne of C entering the river network, with a 5th–95th percentile range of 2.3–4.4 tonnes CO_{2eq}/tonne of C entering the river network. This consideration of the role of the actual water treatment works will be an underestimation as no role for DIC has been considered and many water treatment works adjust the pH of waters prior to treatment and that adjustment could cause loss of CO_2.

The WTR once produced by a water treatment works will continue to degrade. In the UK, 58% of the WTR was disposed of to landfill; 29% was disposed of via sewage treatment; and the remaining 13% was disposed to agricultural land and brick and cement production [*Water UK*, 2014]. The WTR and potential emissions would be different in each one of these disposal pathways but in comparison to fate in the fluvial network there is a critical question of timescales. The median in-stream residence time of water at median flow in the UK has been estimated as 26.7 h and even if the source of most DOM is considered to be in headwaters then the residence time of DOM in the UK may only be a matter of days. However, the in-stream residence time of particles would be expected to be far longer.

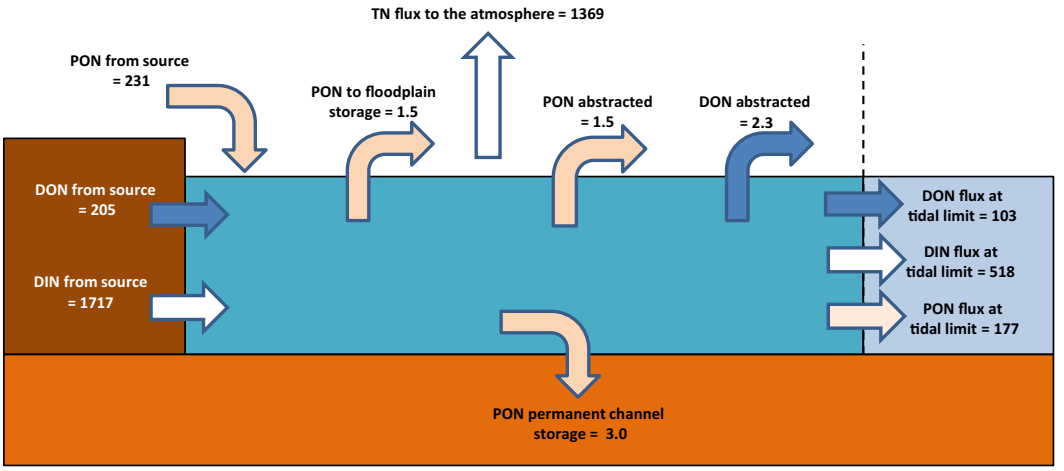

Figure 4. Schematic representation of the fluvial fluxes of nitrogen into and out of UK rivers based upon median values reported in Table 7.

Table 8. The Greenhouse Gas Impact of UK Rivers, Where X = N, C or CO_{2eq}

Flux Pathway	Median (ktonnes X/yr)	5th to 95th Percentile Range (ktonnes X/yr)
N_2O to atmos.	34	10–67
GWP of N_2O	10,040	3,014–19,634
CH_4 to atmos.	46	23–79
GWP of CH_4	1,112	556–1,907
CO_2 to atmos.	3,380	2,704–4,197
GWP of CO_2	12,406	9,925–15,405
GWP of C	13,415	10,556–17,087
Total fluvial GWP	23,868	15,820–32,998
GWP of fluvial OM	14,161	11,141–17,667
Export pathway	Median (tonnes X/km^2/yr)	5th to 95th percentile range (tonnes X/km^2/yr)
Total fluvial GWP export	98	65–135
GWP of fluvial OM export	59	46–73

The circumstances of the UK are not necessarily typical of that elsewhere in the world. First, removal of organic matter in water treatment will only be a phenomena of those countries where there is centralized, municipal water treatment where the removal of particles and the treatment, however, we might reasonably conclude that such treatment facilities are in place for OECD countries. Within the OECD countries in 2014, there were 1.07 billion people and if it were assumed that this population has access to water treatment as it is in the UK then water treatment is removing 920 ktonnes C/yr. The values reported here are also dependent on the density of population, in effect the impact of water abstraction is per capita but other components of the fluvial flux are not and rather are controlled by area, soil, land-use, and topography. Finally, the fluvial flux of carbon is often dominated by the presence of organic-rich soils [*Worrall et al*., 2012a, 2012b] and the impact of water abstraction on fluvial carbon fluxes will be greatest when abstraction has to occur on water sources with high DOM and POM, therefore water abstraction will be more of an issue for the fluvial carbon flux in boreal and subboreal countries.

5. Conclusions

This study has been able to estimate the impact of water abstraction on the fate of fluvial carbon through the UK. The median estimate of removal by water abstraction in the UK is equivalent to 0.76 ± 0.58 kg C/ca/yr (or 46 ± 21 ktonnes C/yr), and 0.07 ± 0.04 kg N/ca/yr (4.0 ± 1.8 ktonnes N/yr). The GHG impact of UK fluvial carbon fluxes, including the impact of water abstraction and the treatment of the carbon in that abstracted water, was 3.5 ± 1.1 tonnes CO_{2eq}/tonne of C entering the fluvial network. For the UK, this equates to a greenhouse gas warming potential of the river network of 16,102 ± 4000 ktonnes CO_{2eq}/yr or 2.7% of current UK greenhouse gas emissions. The removal of carbon via water abstraction represented between 0.9 and 1.3% of total organic carbon fluvial flux from the UK.

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